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MATERIALS DEGRADATION STUDIES FOR HIGH TEMPERATURE STEAM ELECTROLYSIS SYSTEMS

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Experiments are currently in progress to assess the high temperature degradation behavior of materials in solid oxide electrolysis systems. This research includes the investigation of various electrolysis cell components and balance of plant materials under both anodic and cathodic gas atmospheres at temperatures up to 850°C. Current results include corrosion data for a high temperature nickel alloy used for the air-side flow field in electrolysis cells and a commercial ferritic stainless steel used as the metallic interconnect. Three different corrosion inhibiting coatings were also tested on the steel material. The samples were tested at 850ºC for 500 h in both air and H_2O/H_2 atmospheres. The results of this research will be used to identify degradation mechanisms and demonstrate the suitability of candidate materials for long-term operation in electrolysis cells.

I. INTRODUCTION

High temperature steam electrolysis (HTSE) for the production of hydrogen using solid oxide electrolysis cells (SOECs) is the subject of recent research and development efforts.[1,2] A single electrolysis cell consists of an anode, cathode, and a solid oxygen ion conducting electrolyte. In the planar configuration, these devices can be arranged in multiple-cell stacks with the individual cells joined by electrically conducting interconnects. The operating temperatures of SOECs (as high as 800-900°C) and the atmospheres within the cell (steam-hydrogen feed gas mixtures on the cathode side and oxygen-rich gas mixtures on the anode side) can be very demanding from a materials degradation standpoint. The commercial use of SOECs will require extended operation (≥ 40,000 hours), and the materials must exhibit minimal degradation over these time scales. Corrosion of the various electrolytic cell components will result in reduced performance and shortened device lifetimes, and therefore presents significant challenges.

While research on SOEC materials has been somewhat limited in the technical literature, the electrolysis cell architecture, materials of construction, and operating conditions bear many similarities to solid oxide fuel cells (SOFCs), which have been the subject of extensive R&D over the last 20 years.[3,4] Therefore a great deal of the materials development for fuel cells has direct applicability to SOECs.

Interconnect materials must be electrically conductive, resistant to high temperature corrosion, impermeable to the anodic and cathodic gases, and have a thermal expansion coefficient match to the other cell materials, most notably the solid oxide electrolyte (typically stabilized zirconia). Both ceramic and metallic materials have been explored as interconnect materials.[5,6] Metallic candidates have the advantages of mechanical strength and ease of manufacture. The development of metallic interconnect materials has focused on materials that form stable, adherent oxide scales under the SOEC operating conditions, which can act as an effective barrier to further oxidative corrosion. However the additional requirement of electrical conductivity means that protective oxide layers must also have relatively high conductivities. This requirement rules out alloys that form alumina- or silica-based oxide scales, as the resistivity is much too high, and has resulted in a focus on materials forming chromium oxides. The primary metallic candidates for interconnects include high temperature nickel alloys and certain high-chrome ferritic stainless steels.

In addition to metallic interconnects, certain cell stack designs require a separate metallic flow field to be employed.[7] These materials are subjected to the same cathodic and anodic gas mixtures and temperatures as the interconnects. Nickel is effective as a cathode-side flow field, while Ni-Fe-Cr alloys are candidates for the anode side.

Outside of the electrolytic cell, HTSE system components such as gas manifolds will be exposed to super-heated H_2O/H_2 and air/O_2 gas mixtures, and therefore will be subjected to similar corrosion processes as in-cell materials. Metals considered for these balance of plant applications will include commercial high temperature oxidation resistant alloys for service in oxygen or steam/hydrogen atmospheres. Possible candidates include high temperature nickel alloys such as Haynes 230 and Inconel 617.

The Idaho National Laboratory (INL) has an advanced research and development program on bench-scale SOEC systems and is preparing for continued

testing on larger lab-scale and pilot-scale systems.[7,8] Integral to the scale-up of this technology is an understanding of materials degradation in prototypic materials over long time scales. This paper describes the initial results of high temperature isothermal materials degradation studies currently in progress, as well as a description of planned work.

II. EXPERIMENT DESCRIPTIONS

II.A. Materials

The materials used in this study consist of (i) a commercial ferritic stainless steel containing 18–20% Cr (designated FSS here), and (ii) a Ni-Fe-Cr alloy (designated Ni1 here). The stainless steel is used for interconnect and edge rails and the nickel alloy is used as the air-side metallic flow field in experimental bench-scale electrolytic cells. Several proprietary coatings, designed to improve corrosion resistance by formation of relatively high electrical conductivity oxides, were applied to the FSS samples. These coatings consist of rare-earth element treatments, either alone or in conjunction with additional ceramic phases. The coatings are identified in the results and discussion section as C1, C2, and C3.

The sample specimens were thin sheets (thickness $\leq$ 1 mm) cut into approximately 1 cm x 1 cm coupons. Prior to corrosion testing, bare metal samples were ultrasonically cleaned in acetone. The coated steel specimens were tested in the as-coated condition.

II.B. Single Atmosphere Corrosion Tests

The experimental testing involves sample coupons exposed to various gas mixtures at temperatures up to 850°C. Experiments have been performed for up to 500 h currently; future testing will include experiment durations up to 8,000 h to investigate long term materials degradation. Steam/hydrogen gas mixtures simulate the cathode-side atmospheres of electrolysis cells, while air/O_2 mixtures simulate the anode-side when air is used as the sweep gas. In current experimental cells, the H_2O/H_2 ratio in the cathodic gas mixture will typically be ~10 at the cathode inlet, and ~1 or less at the outlet. Oxygen partial pressures on the anode side of the cell can range from ~0.21 (i.e. dry air) at the inlet to ~0.5 at the outlet.

The sample materials are placed in a ZrO_2 boat inside a Hastelloy tube, which runs through a tube furnace. Steam/hydrogen mixtures are produced by flowing H_2 in an N_2 carrier gas through a temperature controlled water bath. The H_2/N_2 stream is produced by blending the two gases in a manifold with the individual flowrates controlled by mass flow controllers. The nitrogen carrier gas is used here to mimic the conditions employed in the current electrolysis cell experiments.[7] The $H_2O/H_2/N_2$ mixture is then directed past the samples in the heated furnace. The total gas flow rates range from approximately 500 to 3000 sccm. Heat tracing on the gas supply tubing prevents H_2O condensation prior to injection into the furnace. Air/O_2 mixtures are produced by blending the two gases at the desired flow rates using a mixing manifold with mass flow controllers.

During the experiments the samples are removed from the furnace at periodic intervals to measure the weight change.

II.D. Materials Characterization

Following the corrosion test, the samples are characterized to determine corrosion scale thickness and morphology and to identify the crystalline phases present and the elemental compositions.

The morphology and chemistry of corrosion scale is characterized using SEM and EDS analysis. Scale thickness is characterized using SEM cross-section analysis. Grazing incidence x-ray diffraction is used to identify specific crystalline phases formed on the materials surfaces.

Because of the requirement of good electrical conductivity on materials in multiple cell stacks, the area specific resistivity of oxide layers on materials considered for interconnects or flow fields will be determined as a function of temperature after corrosion testing. These measurements will be accomplished with a high temperature electrical test apparatus (Fig. 1). Each test sample is placed within an electrically insulating ceramic holder with platinum electrodes on both sides. Platinum wire inside of the ceramic holders connects the electrodes to the outside of a simple clam-shell furnace for probe connection. The ceramic holders are spring tightened (not shown) to insure good contact between electrodes and sample at all temperatures. Platinum paste is applied to both faces of the sample to enhance electrical contact over the entire test temperature range.

PC4 cell cable probes (Gamry Instruments) connected the platinum wire to a potentiostat used in conjunction with Gamry Instruments software (FrameWork1 "DC105") to perform electrical resistivity measurements at all temperatures. The potentiostat controls the voltage difference between the test sample electrodes (the working electrode) and an internal reference electrode allowing the current flow between the working and auxiliary electrodes to be monitored. Electrical resistance is derived from the applied voltage and measured current through the samples. A schematic of the measurement is shown in Fig. 2.

The area specific resistance (ASR) of the oxide scale has the units of Ω cm^2 and is calculated using the following equation:

$$ASR = \left(\frac{R \cdot A}{2} \right) \qquad \text{(Eq. 1)}$$

where R is the measured resistance (Ω) and A (cm^2) is the electrical contact area between the Pt electrode and the sample. Dividing by 2 accounts for the fact the resistance measurement is performed across two oxide scale layers connected in series. The resistance of the alloy substrate and current leads are considered negligible compared to the resistance of the oxide scale.

With this system the electrical resistance can be measured at temperatures of up to 1000º C. The high temperature measurements are conducted in a flowing argon cover gas to minimize corrosion of the samples during testing.

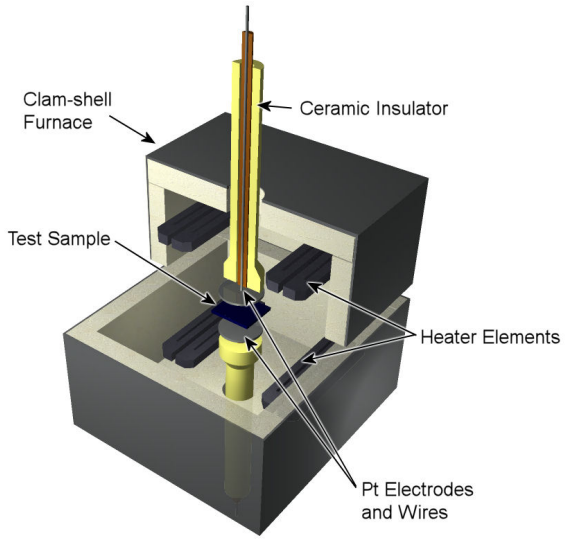

Figure 1. High temperature area specific resistivity measurement apparatus.

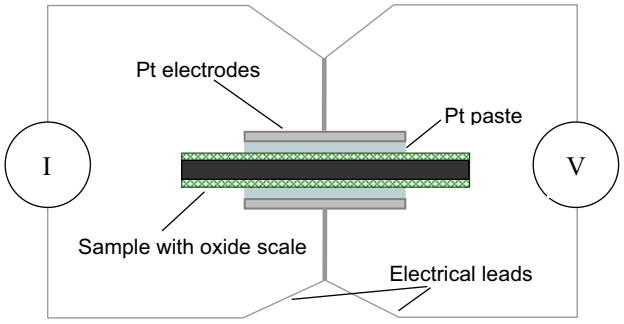

Figure 2. Schematic diagram of area specific resistivity meausurement.

III. RESULTS AND DISCUSSION

Several single atmosphere 500 hour tests have been completed. The experimental conditions of these tests are given in Table I. Tests 1 and 2 correspond to H_2O/H_2 ratios of 5.3 and 0.5, respectively.

Table I. Conditions for 500 hour corrosion tests.

Test #	Temp. (°C)	Gas mixture
1	850	46.9%H_2O/8.9%H_2/44.2%N_2
2	850	18.5%H_2O/37.1%H_2/44.4%N_2
3	850	Dry air

The weight gain data taken at 500 h are shown in Figure 3. The weight gain data is used as a measure of corrosion rate by the growth of oxide scale on the samples.

In all test atmospheres the weight gain of the uncoated steel was higher than the nickel alloy. The differences in weight gain for Ni1 in the three different test atmospheres were almost negligible. The highest weight gain for the FSS sample was in $H_2O/H_2 = 5.3$.

The largest weight gains for all of the coated FSS samples were in air, where the differences between the uncoated and coated FSS were the least significant. The best performing coating (i.e. the largest reduction in weight gain compared to the bare FSS sample) in air was C2. On the other hand, it appears that the coatings were more effective at reducing corrosion rates in H_2O/H_2 atmospheres. Weight gains for coated FSS samples in both H_2O/H_2 mixtures were reduced by approximately 50% or more compared to bare FSS. The best performing coating was C3, although the differences in coating performance in H_2O/H_2 mixtures were minor.

The XRD analysis of exposed samples from Test 1 ($H_2O/H_2 = 5.3$) indicated that the predominant phases forming on the Ni1 sample surface were chromium oxide (Cr_2O_3) and chromite ($FeCr_2O_4$), while in the case of the bare FSS material magnetite (Fe_3O_4) was formed.

The data obtained to date indicate that the protective coatings significantly reduce corrosion rates in H_2O/H_2 atmospheres, but the improvement is less pronounced in air, and in some cases (coated C1) is negligible. Full interpretation of the weight data will be better performed when the x-ray and microscopy data are available from all samples. Also, the planned ASR measurements will indicate which material/coating combinations exhibit the highest resistivities.

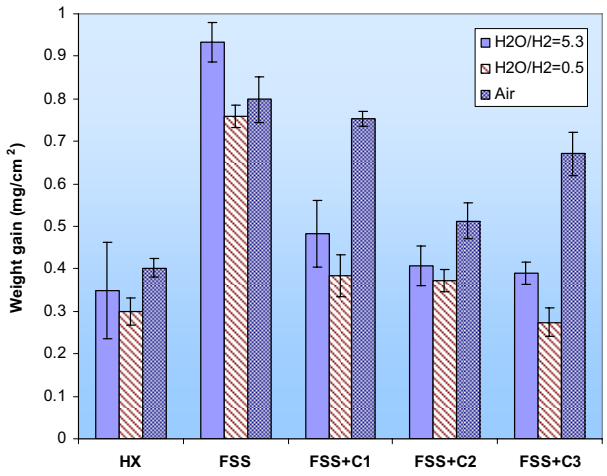

Figure 3. Weight gain data for 500 h exposure in air and steam/H_2 mixtures at 850°C.

IV. FUTURE WORK

Separate corrosion experiments will also be performed under conditions similar to those described above in a thermal gravimetric analyzer (TGA) to more accurately measure isothermal weight gain of small samples as a function of time. This data will be used to better determine the kinetics of oxide scale growth and obtain activation energies for the corrosion processes for different alloys and alloy/coating combinations. The experimental TGA system will allow the use of the same corrosive atmospheres (i.e. air/O_2 and $H_2O/H_2/N_2$).

During elecrolytic cell operation, the interconnects are exposed simultaneously to the cathode-side gas mixture on one side and the anode-side gas mixtures on the other. Previous work on materials corrosion issues in solid oxide fuel cells has indicated that such dual atmosphere conditions can result in unique corrosion processes compared to single atmosphere corrosion.[9] Dual atmosphere corrosion of metallic interconnect materials will also be pursued as part of this study. A unique corrosion cell is currently being designed for this purpose, and the existing gas supply system is prepared to supply both H_2O/H_2 and air/O_2 mixtures to the cell.

Ongoing work in this area will also be expanded to include candidate high temperature electrolysis balance of plant materials, with corrosion experiments designed to focus on long term materials degradation. Understanding these degradation processes will be critical in the development and successful operation of large-scale electrolysis plants. Candidate materials will include several nickel-based alloys.

V. SUMMARY

Current work on solid oxide electrolysis cell materials was described and initial data on metallic interconnect and flow field material corrosion was presented. Several rare-earth based coatings have been demonstrated to significantly inhibit corrosion in H_2O/H_2 atmospheres and continuing work will allow complete characterization of the oxide scales that grow on these samples during high temperature corrosion.

Future work will include an investigation of dual atmosphere corrosion studies on SOEC metallic interconnect materials, and long term degradation studies on balance of plant materials.

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